Probiotics for sustainable leather – sustainable alternatives

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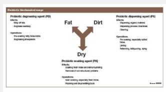
Since the introduction of industrial processing, relatively few innovations have taken place in tanneries to adequately address sustainability. A recent study by Proviera's Juan-Carlos Castell and Claus Reineking of Stahl finds some natural, probiotic alternatives to traditional, chemical-heavy methods.



Processing hides and skins generates very high amounts of wastewater and solid residues, many of which can be valuable for other applications if they are not contaminated with chemicals. For example, 1t of bovine salted hide requires 500kg of chemicals to produce half that weight of finished leather.

Tanners must therefore manage huge excesses of non-leather materials to avoid pollution. When applying R3 environment strategies, the main potential actions focus on several areas:

- Reducing chemicals through efficient methods that optimise dosing, and ensure full exhaustion of processing agents and eliminate or improve efficiency of auxiliaries. Consequently, reduction of effluent charges will be expected by improving COD and BOD values, salinity and toxicity.
- Reusing some chemical auxiliaries that remain in the effluents and solid residues that could be applied in the leather process as raw material (retanning agents, for example).
- Recycling solid residues by deriving protein, fats and other components to other industries of high value like cosmetics, medicine and food.

Biotechnology is now suitable for supporting tanners implementing R3 environmental strategies by reducing the need for synthetic chemicals, improving exhaustion and adding value to by-products. Additionally, technology based on probiotics leads to other sustainable benefits, like a natural fermentation process, fully renewable raw material, 100% biodegradable and safe biochemicals, reduction of carbon footprint and, at the same time, improvement of the quality of the leather articles.

The word 'probiotic' has been in common use for more than 25 years and definitions have been refined, but it is most commonly used to describe live microorganisms that confer health benefits. It is on the cutting edge of developing technology for a range of applications, including human health, agriculture and industrial waste management, as well as leather and textile processing.

Probiotics use beneficial and effective microbes to repopulate environments with healthy microorganisms. Raw materials are carefully fermented with a probiotic mother culture resulting in metabolites composed of a mixture of biochemicals. The mother culture is a selection of microbes grown in 'consortia', in a process of co-growth that combines multiple strains during production. The microorganisms become a small ecosystem that is much more resilient and capable of working together. This is similar to how microorganisms survive in nature, where strains never exist in isolation or as a pure culture.

Microbes are always interacting with each other. Significant differences can be noted when comparing the innovative and disruptive probiotic technology with traditional chemical synthesis:

- fermentation is a complete natural bio-reaction and does not require additional sources of external energy; the carbon footprint is therefore minimised and does not cause greenhouse gas emissions
- biochemicals derived from fermentation using probiotics do not have any potential toxicological effects (unlike synthetic chemicals) and are non-corrosive
- probiotic technology uses raw materials from renewable and sustainable resources, and do not depend on other industries like

- crude oil
- fermented biochemicals are completely biodegradable.

Each microbe strain carries specific properties together with its metabolites that enable them to offer functions such as degreasing, dispersing and conditioning. These properties are derived by the cautious use of additives, which are processed using specific manufacturing systems.

Probiotic biochemicals

Probiotic biochemicals are hydrotropes and possess the ability to increase the solubility of organic molecules in water. The composition includes some hydrophilic and lipophilic, like typical surfactants, but they contain a very small hydrophobic fraction that does not allow aggregates, such as micelles, to form. Dirt, dung, waxes, phospholipids among soluble or non-structured proteins such as hyaluronic acid, dermatan sulphate, elastin, glyco-amino-glycans and globulins in the hides and skins are cleaved off, solubilised and dispersed into the floats during the first stages of the leather processing, mainly in the soaking operations. Processing chemicals, such as tanning and retanning agents, fatliquors and dyes, are dosed in water solutions to bond the functional groups of the collagen for tanning or to provide all physical properties to the leather articles in wet-end operations.

Besides, hydrotropes are recognised as excellent wetting agents when they are in contact with collective structures, such collagen fibres. They allow media to accept water, working like surfactants to break the surface tension of the fluid to help it transfer from particle to particle. Consequently, water molecules can permeate the fibrous collagen structure into the fibril and microfibril tissue, break hydrogen bonds and activate the protein functional groups. This wetting effect is associated with a slight lyotropic swelling and relaxes the fibre structure, allowing the fixation of ionic substances.

Probiotic biochemicals have strong capabilities to eliminate, or at least to reduce and combine, all kind of soaking and wetting agents, enzymes, degreasers, dispersing agents, solvents, dye auxiliaries and ammonia, all of which are used extensively in beamhouse and wet-end operations. Most of these agents contribute to effluent pollutants and are not fully biodegradable.

Because their action aims to reduce superficial tension, surfactants require additional washes so as to be removed from the leather. Potentially, probiotic biochemicals save water consumption as they do not foam.

Probiotic biochemicals are compatible with all chemicals used in the leather- making process and do not need to adjust to conditions – such as pH and temperature – beyond those required in the manufacturing operations.

Except under unusual conditions – such as deficient preservation or long soaking – the soaking operation using probiotics biochemicals is free of bactericides and can reduce bad odours or putrefaction.

Although the need for bactericides in soaking depends on the totality of all the prevailing conditions, they are habitually added in the tanneries. Handling biocides requires adequate safety equipment for increased effluent charges like COD and the impact on the efficiency of the biological reactors in the wastewater treatment plants.

Probiotic biochemicals cannot be considered as bactericides, although, they are capable of delaying for a limited time the harmful consequences of certain putrefying bacteria like bacillus, E. coli and listeria, because of bacteria competition exclusion, or quorum sensing.

Material and methods

This study compiles a set of trials carried out on different materials in industrial drums and pilot plants, from salted to fresh hides from different origins, and sheepskins and goatskins and wet-blue. All demonstrations followed the same processing scheme, and the doses and conditions were adjusted as described.

Three different probiotic biochemicals (patent pending) have been designed to be differentiated by their hydrophilic-lipophilic-balance (HLB). This was intended to obtain higher soaking, dispersing or degreasing properties. The products were named as a probiotic soaking agent (PK), probiotic dispersing agent (PS) and probiotic degreasing agent (PD).

Wash and presoak

The objective was the removal of dirty substances from animal (manure, blood and so on) and preservation substances (salt and biocides). In salted hides or skins, additional washes are used to reduce salt concentration and provide superficial degreasing to eliminate external waxes and phospholipids on the hair and epidermis. Dosing was on green weight:

- Washes: 0.10% PK and 0.00–0.05% PD. No pH adjustment.
- Presoak: 0.20–0.50% PS, higher in salted raw material; 0.00–0.05% PD. No pH adjustments.

The probiotic biochemicals replaced surfactants and enzymes (soaking agents) and degreasers. Biocides were not added.

Main soak

The objective was to rehydrate hides and skins, and bring them to a flaccid condition for subsequent operations and the removal of some globular proteins that will interfere with the tanning process. Dosing was on green weight:

- 0.30–0.50% PK. Higher on fresh raw material; 0.0–0.3% PS.
- products were added prior to alkalis to adjust pH (8.5–9.5) for liming.
- This offers alternatives to most chemical soaking agents, either surfactants or enzymes.

Unhairing/liming

The objective was the removal of hair and further completion of globular proteins by the action of the alkali. Dosing was on green weight:

- 0.2% PD, prior to lime and sulphide.

This eliminates or reduces the use of amines, organic reductive agents and polyphosphates, all of which are typical auxiliaries in the unhairing and liming processes.

Degreasing

The objectives was to strip off natural fats from adipose tissue, especially inside skins, to disperse natural fats in the float and solubilise them by emulsification with surfactants or hydrolysation under the action of lipases. Tests were carried out after deliming, before or during the bating for bovine hides, goat skins and sheepskins, or after pickling/depickling for sheepskins. Posterior washes, in most cases, used non-ionic surfactants with a high emulsifying effect. Dosages were based on lime pelt weight:

- 0.5–3.0% PS; 3.0–6.0% PD, depending of the natural fat content. Degreasing can need one to three washes.

Probiotic biochemical can replace – or at least drastically reduce and have synergies with – degreasing agents based on blends of surfactants and lipases. They can remove the need for solvents, as natural fats can easily be stripped from pelts.

Wet-end

The objectives were the preservation and conversion of hides and skins into useful commercial articles, and to achieve resistance to bacterial attack and to high temperatures. Typical tanning methods are mineral (mainly chrome), vegetable and organic (aldehydes and oils). Dosing was on limed pelt weight:

- 2.0–5.0% PS.

This provides alternatives to dispersing agents and tanning auxiliaries.

Wetting back/washing

The objectives were to rehydrate tanned leather, wet-blue, wet-white or vegetable-tanned after a period of piling or storage; to wash leather to obtain regular surface and obtain regular rehydration; and chelating metallic cations leached from mineral tanning. Dosing was on shaved weight:

- 0.5–2.0% PS, depending on cleanness of tanned leather; 0.0–1.0 % PK (depending on dryness); 0.0–1.0% PG, depending on grease content.

Probiotic biochemical can replace surfactants, ammonia and oxalic acid commonly used for washing and cleaning up wet-blue, wet-white or vegetable leathers.

Retanning/fatliquoring/dyeing

The objectives were to add and fix processing chemicals – such as retanning agents, fatliquors and dyes – to achieve the final features of the leather articles. Dosing was on shave weight, or double on crust (pearl) weight:

- 0.5–2.0% PS or PG

This gives alternatives to surfactants, ammonia and dyes derived from naphthalene sulphonic and ethoxylated amines.

Results

Innovative, all-natural probiotic biochemicals can replace traditional chemicals in leather tanning. Using unique probiotic formulations, the biochemicals are able to improve leather quality, increase yield, lower operating costs and reduce environmental pollution.

Rawhides and skins vary in animal type (bovine, sheep, pig and so on) and across breeds, fat content (prefleshing-mechanical removal of fat from rawhide, different animal types have different levels of natural fat and other characteristics), origin (temperature is the largest indicator for fat content: the colder the environment, the more fat), method of preservation (salted, sun-dried, chemical preservatives, raw) as well as cleanliness (rawhides are covered in blood, dung, dirt and so on).

Regional variation

Rawhides vary by region and characteristics influence the application rate of probiotic biochemicals. In addition to raw hide characteristics, each tannery will follow a unique process to produce their desired leather. This includes the brand and quantities of chemicals used in each stage; process time in each stage; machinery (drums versus paddles); the speed of drum rotations; water saving methods; mechanical actions; the sophistication level of the tannery (fully automated or labour); environmental regulations; hair-saving methods or dissolved hair systems; the type of tanning (chrome or vegetable); the presence of a wastewater treatment plant; and climate. Each of these characteristics influences the application rate of probiotic biochemicals.

Beamhouse benefits

Probiotic biochemicals perform as well as the best of chemicals/enzymes and are flexible in application. They can be applied at wide pH and temperature ranges and are non-harmful (safe for tannery workers and leather article consumers). The figure on page 25 describes each of the products used in the trials and the effects on the leathers.

They can be applied in different stages of the leather-making process. The beamhouse benefits are as follows:

- Wash/presoaking: avoid putrefaction and bad odours without bactericides. Reduce the soaking time if raw material is very dry. Cleaning and degreasing raw hides/skis surface. Reduction of COD values or increase of BOD/COD ratio. No foaming.
- Main soaking: uniform wetting back. Hides and skins are very clean with slight lyotropic swelling that enhances fibre sponginess and relaxation. Reduction of soaking time when rawhides or skins are dry or became very dry after a long period of storage time. Reduction of COD values or increase of BOD/COD ratio. No foaming. Typical results of COD analysis of the soaking floats give values ranged between 25kg O_2/ton of hide to 35kg O_2/ton of hide. With the use of probiotic biochemicals the range was reduced to 15kg O_2/ton of hide to 25kg O_2/ton of hide.
- Unhairing/liming: improve dispersion of lime and open wrinkles. Avoids draw marks, and limed pelts are more relaxed and flatter. Easier removal of scud and hair roots. This influences the uptake of tanning agents; for example, higher chromium(III) oxide (Cr_2O_3), and potentially improves quality sorting of leather and increases yield.
- Degreasing: probiotic biochemicals improve the efficiency of the degreasing proses, even though emulsifiers or lipases must be used in high fatty raw materials. Natural fats impact on the COD and BOD values of the effluent, and they can be reduced with probiotics biochemicals.
- Tanning: dispersing of tanning agents to achieve leather more uniform in fullness among different parts, including flanks. Better fixation of tanning agents and potential reduction. Better penetration of tanning agents. Increase of shrinking temperature in wet-white leathers.

The benefits to the wet-end process as desribed by this study are:

- Washing/wetting back: clean and uniform surface on the leather. The leather is of a brighter and cleaner appearance than standards. Additionally, probiotic biochemicals do not impact water resistance when manufacturing waterproof articles. No foaming.
- Retanning/fatliquoring/dyeing: Better dispersion and exhaustion of leather-processing chemicals. Brighter and more-uniform colours. Better shade build-up and fault coverage from dyestuffs. Additionally, probiotic biochemicals do not impact water resistance when manufacturing waterproof articles. Potential reduction of nitrogen and sulphates on effluent when probiotic biochemicals replace auxiliaries that highly contribute to these contaminants.

Variables that influence the results are the chemicals already used in the tannery, origin of rawhides, preservation methods, mechanical action and so on. COD processes with probiotic biochemicals were gathered from trials on wet-salted bovine hides with better results.

The potential reduction of COD obtained for the whole process, from wet-salted raw bovine hides up to finished leather, was up to 24%.

A probiotic future?

Groundbreaking probiotics technology enables unmatched processing results across various industries with no impact on environment. Metabolites from the proprietary fermentation process of natural ingredients from renewable sources with probiotics are characterised by their hydrotropic properties and capable of delaying the damages caused by bacterial putrefaction, as well as the bad odours produced.

Such qualities offer tanners an exceptional opportunity to replace some chemicals auxiliaries based on chemical synthesis of oil derivate with natural, biodegradable and sustainable alternatives without amending existing manufacturing processes.

The application of probiotic technology to prepare hides and skins for tanning and the successive operations of leather-making improves the quality of the leather articles, saves water consumption and costs while reducing environmental impact.

Compared with traditional chemical auxiliaries, probiotic biochemicals are able to transfer water molecules into the smallest interspaces of the fibril collagen structure up to the protein chain, cleave off and disperse substances from hides and skins not suitable to be converted in leather, solubilise organic material and improve the uptake of the reagents that confer final leather properties.

This work demonstrates the potential of the probiotic biochemicals in different stages of leather manufacturing for improving leather quality and reducing effluent pollutants.

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